Voltammetric Studies at Glassy Carbon Electrodes in Sulfuryl Chloride Solutions

Wishvender K. Behl

U.S. Army Electronics Technology and Devices Laboratory (ERADCOM), Power Sources Division, Fort Monmouth, New Jersey 07703

Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 127, No. 7, July 1980
Printed in U.S.A.

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U.S. Army Electronics Technology and Devices Laboratory (ERADCOM),

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ABSTRACT

The electrochemical reduction and oxidation of sulfuryl chloride in 1M $LiAlCl_4$-SO_2Cl_2 solutions were studied at glassy carbon electrodes using the technique of cyclic voltammetry. It was found that the reduction of chlorine, which is formed by the decomposition of sulfuryl chloride, precedes and obscures the reduction of sulfuryl chloride. Thus, in chlorine-rich solutions, sulfuryl chloride reduction peak in the cyclic voltammograms is completely masked by the chlorine reduction peak. However, in solutions saturated with sulfur dioxide, the chlorine reduction peak is relatively smaller than the sulfuryl chloride reduction peak. The reduction of both chlorine and sulfuryl chloride leads to the deposition of insoluble lithium chloride at the electrode surface and results in its passivation. The electrochemical oxidation of $LiAlCl_4$-SO_2Cl_2 solutions leads to the formation of chlorine, first by the oxidation of $AlCl_4^-$ ions followed by the oxidation of sulfuryl chloride.

During the past few years, a number of studies have been reported on the ambient temperature lithium-inorganic electrolyte battery systems. However, only a few of these studies have been devoted to the lithium-sulfuryl chloride system. The scarce literature includes studies of the discharge characteristics (1-4) and discharge reaction stoichiometry (4) of lithium-sulfuryl chloride cells, conductivities (5), and voltammetric reduction of sulfuryl chloride (6) in $LiAlCl_4$-SO_2Cl_2 solutions. The electrochemical reduction and oxidation of sulfuryl chloride in 1M $LiAlCl_4$-SO_2Cl_2 solutions and in solutions containing excess of chlorine or sulfur dioxide were also investigated in this laboratory employing the technique of cyclic voltammetry. This paper summarizes our results.

Experimental

The preparation and purification of lithium tetrachloroaluminate have been described elsewhere (7). Sulfuryl chloride (Matheson, Coleman and Bell Company) was refluxed over lithium metal and distilled as colorless liquid. However, on storage, the color slowly changed to light yellow. Solutions of lithium tetrachloroaluminate in sulfuryl chloride were light yellow in color.

A three electrode system was used for all measurements. The reference (1 × 5 cm) and counter (3.5 × 6 cm) electrodes were both made by pressing lithium ribbon (0.38 mm thick; Foote Mineral Company) onto a nickel screen. The reference electrode was contained in a Pyrex tube (10 mm diam) with a coarse porosity fritted glass bottom. Both the reference and the counterelectrodes were thoroughly washed with carbon tetrachloride before use. The working electrode consisted of a 3.18 mm diam glassy carbon rod (Beckwith Carbon Company) heat-sealed in a shrinkable Teflon tubing and the end ground flush with the seal so as to expose the cross section of the rod. The glassy carbon electrode was then polished to a mirror finish using a 0.3 μm size powdered alumina and had an area of 0.079 cm^2.

All experiments were performed inside a Dry-train, Dry-lab (Vacuum Atmosphere Corporation) in a pure dried argon atmosphere. Other experimental details (8-10) were similar to those used for the voltammetric studies in phosphorous oxychloride and thionyl chloride solutions.

* Electrochemical Society Active Member.
Key words: electrolyte, battery, voltammetry.

In order to obtain reproducible voltammograms, the passivating lithium chloride film on the working electrode was dissolved, after each scan, in acidic $AlCl_3$-SO_2Cl_2 solution followed by washing with sulfuryl chloride and carbon tetrachloride. The electrode was then wiped clean and mechanically polished. The electrode could also be cleaned, *in situ*, by holding the electrode potential[1] at ~ 4.5V for 1-2 min. However, this procedure was not employed since it led to the contamination of the solution by the oxidation products, namely, chlorine, aluminum chloride, etc. (see Discussion).

Results

Typical cyclic voltammograms obtained in 1M $LiAlCl_4$-SO_2Cl_2 solution, through which pure dried argon was bubbled for 16 hr, at a scan rate of 0.1 V/sec, are presented in Fig. 1. Voltammogram A was obtained by scanning the electrode from 4.0 to 0.25V and voltammogram B by scanning the electrode from 4.0 to 5.0V. Cyclic voltammogram A shows a large increase in cathodic current beginning at ~ 3.6V with a shoulder (peak I) at ~ 3.05V and peak (peak II) at ~ 2.85V. A minor peak (peak III) is observed at ~ 2V before a rapid increase in reduction current is observed at ~ 0.75V. On reversing the direction of polarization at 0.25V, only one small anodic peak (peak IV) is observed at ~ 1.0V. The anodic peak IV is not observed if the direction of polarization is reversed at potentials positive to 0.75V. Similar cyclic voltammograms were observed at scan rates of 0.01 to ~ 0.2 V/sec. At higher scan rates peaks I and II merged together and peak III was slightly more discernible. The peak currents increased with increasing scan rate and peak potentials shifted to less positive potentials.

Cyclic voltammogram B shows a small anodic peak (peak V) at ~ 4.6V before a sharp increase in anodic current is observed at ~ 4.75V. Cyclic voltammograms did not show any reduction peak during the reverse scan. Similar cyclic voltammograms were obtained at scan rates of 0.01-2 V/sec.

In $LiAlCl_4$-SO_2Cl_2 solutions containing excess of chlorine or sulfur dioxide, cyclic voltammograms for the anodic processes were similar to the voltammogram B presented in Fig. 1. However, voltammograms for the cathodic processes were distinctly different from voltammogram A.

Thus, in saturated solutions of chlorine in 1M $LiAlCl_4$-SO_2Cl_2, cyclic voltammograms (Fig. 2) showed only one major reduction peak at scan rates of 0.01-2 V/sec. The peak potential for this reduction peak was closer to the peak potential for peak I in the cyclic voltammograms shown in Fig. 1. While peak II was not observed at all scan rates, the minor peak III became discernible only at scan rates greater than 1 V/sec.

[1] All potentials are reported with respect to lithium reference electrode.

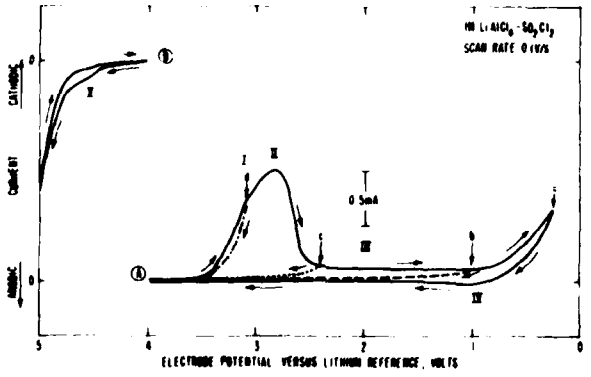

Fig. 1. Typical cyclic voltammograms at glassy carbon electrodes in argon purged 1M $LiAlCl_4$-SO_2Cl_2 solutions at a scan rate of 0.1 V/sec. Roman numerals refer to the different peaks and letters a-d indicate the potential of scan reversal of different sweeps.

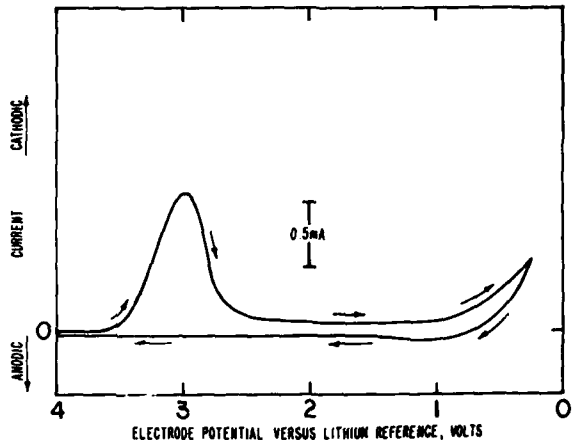

Fig. 2. Typical cyclic voltammograms at glassy carbon electrodes in saturated solutions of chlorine in 1M $LiAlCl_4$-SO_2Cl_2 at a scan rate of 0.1 V/sec.

Typical cyclic voltammograms obtained in 1M $LiAlCl_4$-SO_2Cl_2 solutions, through which sulfur dioxide was bubbled for 16 hr, at a scan rate of 0.1 V/sec are shown in Fig. 3. In these solutions, peak I appears as a small step at ~ 3.3V and peak II is the major peak at ~ 2.75V. Peak III appears as a wide peak beginning at ~ 2V. Again no anodic peak corresponding to reduction peaks I, II, and III is observed on the reverse scan. Similar cyclic voltammograms were observed at scan rates of 0.01-2 V/sec. Again the peak heights for peaks I, II, and III increased with increasing scan rate and peak potentials shifted to less positive potentials. Addition of chlorine to sulfur dioxide saturated $LiAlCl_4$-SO_2Cl_2 solution caused an increase in peak height for peak I (Fig. 4) and a corresponding decrease in peak height for peak II.

Discussion

Sulfuryl chloride is known (11) to decompose to sulfur dioxide and chlorine according to the equation

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2 \qquad [1]$$

Both sulfur dioxide and chlorine are soluble (11) in sulfuryl chloride and remain in solution. While solu-

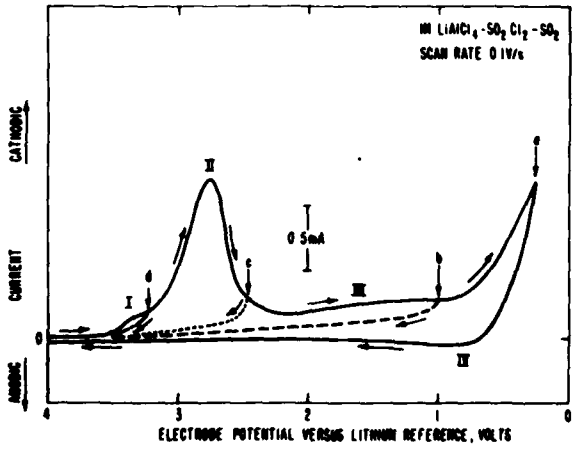

Fig. 3. Typical cyclic voltammograms at glassy carbon electrodes in saturated solutions of sulfur dioxide in 1M $LiAlCl_4$-SO_2Cl_2 at a scan rate of 0.1 V/sec. Roman numerals refer to the different peaks and letters a-d indicate the potential of scan reversal of the different sweeps.

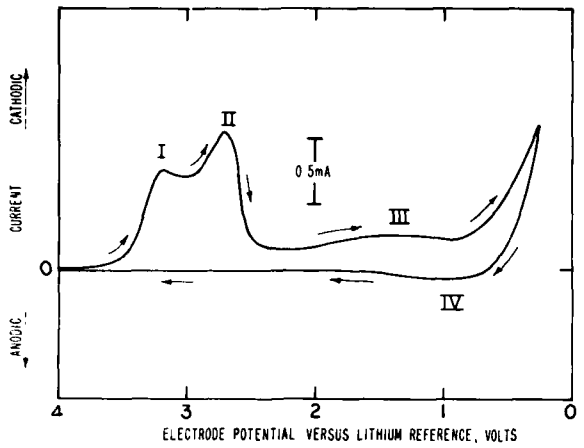

Fig. 4. Typical cyclic voltammograms at glassy carbon electrodes at a scan rate of 0.1 V/sec in 1M $LiAlCl_4$-SO_2Cl_2-SO_2 solutions to which a small amount of chlorine is added.

tions of sulfur dioxide in freshly distilled sulfuryl chloride are colorless, solutions of chlorine are light yellow in color. Solutions of lithium tetrachloroaluminate in freshly distilled sulfuryl chloride were always found to be light yellow in color. Both sulfuryl chloride and its solutions containing lithium tetrachloroaluminate became dark yellow in color on long storage. The yellow color in these solutions is attributed to chlorine which is formed by the decomposition of sulfuryl chloride according to Eq. [1]. It was not possible to completely remove the dissolved chlorine and the yellow color by purging the $LiAlCl_4$-SO_2Cl_2 solutions with argon, especially in the presence of lithium electrodes. It was, however, possible to shift the equilibrium in Eq. [1] to the left by bubbling sulfur dioxide and remove the dissolved chlorine. Thus, the $LiAlCl_4$-SO_2Cl_2-SO_2 solutions were almost colorless.

Electrochemical reduction of sulfuryl chloride.— Cyclic voltammograms (Fig. 1, voltammogram A) obtained in $LiAlCl_4$-SO_2Cl_2 solutions show three reduction peaks before a rapid increase in cathodic current is observed at ~ 0.75V due to the deposition of lithium metal at the electrode surface. On the reverse scan only one anodic peak (peak IV) is observed at ~ 1.0V. Since peak IV is not observed if the direction of polarization is reversed prior to lithium deposition, it may be regarded due to the dissolution of the deposited lithium metal. Similarly, the rapid increase in the cathodic current at ~ 0.75V and the anodic peak IV at ~ 1.0V in $LiAlCl_4$-SO_2Cl_2-Cl_2 (Fig. 2) and $LiAlCl_4$-SO_2Cl_2-SO_2 (Fig. 3) solutions may also be regarded due to the deposition and dissolution of lithium metal, respectively.

In order to identify the other reduction peaks, let us first consider the cyclic voltammograms in $LiAlCl_4$-SO_2Cl_2-SO_2 solutions (Fig. 3). Peak height for peak I in these voltammograms is strongly dependent on the concentration of dissolved chlorine as demonstrated by the addition of chlorine to $LiAlCl_4$-SO_2Cl_2-SO_2 solutions (Fig. 4). Further, if these solutions are allowed to stand for a few hours or if argon is bubbled through the solutions to remove sulfur dioxide, the equilibrium in Eq. [1] is shifted to the right resulting in an increase in the chlorine concentration and a corresponding increase in peak height for peak I. Thus, peak I may be regarded as due to the reduction of chlorine

$$\tfrac{1}{2}\,Cl_2 + Li^+ + e \rightarrow LiCl \qquad [2]$$

The main reduction peak (peak II) in $LiAlCl_4$-SO_2Cl_2-SO_2 solutions may be regarded as due to the reduction of sulfuryl chloride. From a study of the discharge products in lithium-sulfuryl chloride cells, Gilman and Wade (4) have identified lithium chloride as the only solid reaction product. The reduction of sulfuryl chloride may, therefore, be represented as

$$SO_2Cl_2 + 2Li^+ + 2e \rightarrow 2LiCl + SO_2 \qquad [3]$$

The reduction of both chlorine (Eq. [2]) and sulfuryl chloride (Eq. [3]) leads to the deposition of insoluble lithium chloride at the electrode surface and causes its passivation. Since it would require a fixed amount of lithium chloride, at a fixed scan rate, to cover the electrode surface, the combined peak height for peaks I and II remains constant and independent of the chlorine concentration in the solution. Thus, the peak heights for peaks I and II are interdependent and an increase in chlorine reduction peak (peak I) due to increased chlorine concentration results in a corresponding decrease in sulfuryl chloride reduction peak (peak II).

Similarly, peaks I and II in $LiAlCl_4$-SO_2Cl_2 solutions (Fig. 1) may be attributed to the reduction of chlorine and sulfuryl chloride, respectively. Since the chlorine reduction peak appears as the major reduction peak even in $LiAlCl_4$-SO_2Cl_2 solutions purged with argon for 16 hr, it seems likely that chlorine is supplied to the glassy carbon electrode not only by the migration of bulk chlorine but also by the decomposition of sulfuryl chloride at the electrode surface. Thus, at more catalytic surfaces such as platinum (12), the decomposition of sulfuryl chloride at the electrode surface is facilitated and the electrochemical reduction of sulfuryl chloride proceeds mainly through chlorine even in sulfur dioxide saturated $LiAlCl_4$-SO_2Cl_2 solutions.

The minor reduction peak III (Fig. 1 through 4) in the cyclic voltammograms may be assigned to the reduction of sulfur dioxide

$$2SO_2 + 2Li^+ + 2e \rightarrow Li_2S_2O_4 \qquad [4]$$

While peak III is hardly discernible in $LiAlCl_4$-SO_2Cl_2 and $LiAlCl_4$-SO_2Cl_2-Cl_2 solutions, it is easily distinguishable in $LiAlCl_4$-SO_2Cl_2-SO_2 solutions. Since the electrode is already passivated due to the deposition of lithium chloride, the reduction of sulfur dioxide does not occur significantly in these solutions and results in only a very small peak in the cyclic voltammograms.

In order to further differentiate between peaks I, II, and III in the cyclic voltammograms, a small amount of aluminum chloride was added to the $LiAlCl_4$-SO_2Cl_2 solutions previously purged with argon. Since the excess of aluminum chloride increases the corrosion of lithium counterelectrode by dissolving the protective lithium chloride film and eventually results in its complete disintegration, the cyclic voltammograms were recorded immediately after the addition of aluminum chloride and are shown in Fig. 5. The excess of aluminum chloride in $LiAlCl_4$-SO_2Cl_2 solutions also partially dissolves the lithium chloride film on the glassy carbon electrode surface due to complex formation

$$LiCl + AlCl_3 \rightleftharpoons Li^+ + AlCl_4^- \qquad [5]$$

Thus, the electrode surface continues to be partially regenerated during the life of the voltage scan and results in distinct reduction peaks for the reduction of chlorine (peak I), sulfuryl chloride (peak II), and sulfur dioxide (peak III). The peak heights are also slightly higher than those obtained in neutral $LiAlCl_4$-SO_2Cl_2 solutions. Further, due to the partial regeneration of the electrode surface, a small cathodic current is observed during the reverse scan of the cyclic voltammograms (Fig. 5) in contrast to almost no current in neutral $LiAlCl_4$-SO_2Cl_2 solutions (Fig. 1).

In $LiAlCl_4$-SO_2Cl_2-Cl_2 solutions (Fig. 2), the reduction of chlorine completely obscures the reduction of sulfuryl chloride so that only one major reduction

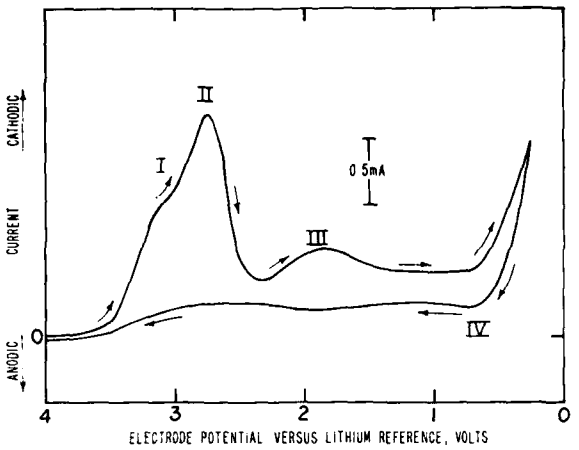

Fig. 5. Typical cyclic voltammograms at glassy carbon electrodes at a scan rate of 0.1 V/sec in 1M $LiAlCl_4$-SO_2Cl_2 solutions containing slight excess of aluminum chloride.

peak is observed in the cyclic voltammograms. Thus, in these solutions, the electrode surface is completely covered by lithium chloride produced as a result of chlorine reduction (Eq. [2]) and is not available for the reduction of sulfuryl chloride and sulfur dioxide. Cyclic voltammograms similar to those presented in Fig. 2 are also obtained in aged $LiAlCl_4$-SO_2Cl_2 solutions. The chlorine concentration in the aged solutions is rather large due to the decomposition of sulfuryl chloride and thus the chlorine reduction peak completely masks the sulfuryl chloride reduction peak. If the excess of chlorine in aged $LiAlCl_4$-SO_2Cl_2 or $LiAlCl_4$-SO_2Cl_2-Cl_2 solutions is removed by bubbling argon, cyclic voltammograms similar to those presented in Fig. 1 (voltammogram A) are obtained.

The total charge passed under peaks I and II of the cyclic voltammograms in $LiAlCl_4$-SO_2Cl_2, $LiAlCl_4$-SO_2Cl_2-Cl_2, and $LiAlCl_4$-SO_2Cl_2-SO_2 solutions was measured as a function of scan rate by integrating the area under the peaks. From the total charge passed, the thickness of the lithium chloride film on the glassy carbon electrode was then calculated taking the density of lithium chloride to be 2.068 g/cm^3 at 25°C. These results are plotted in Fig. 6. The total charge passed and hence the thickness of the lithium chloride film in all three solutions was found to decrease with increasing scan rate. However, at all scan

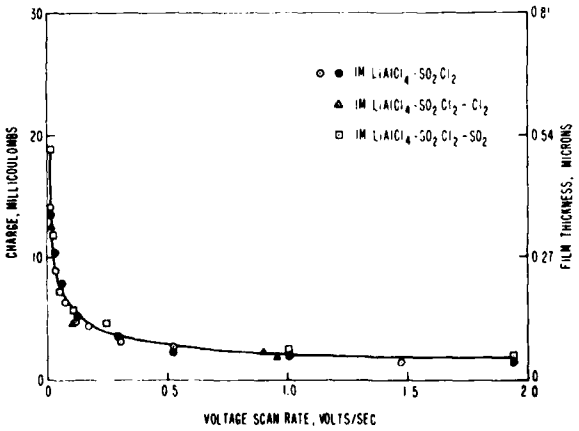

Fig. 6. Total charge passed under peaks I and II of the cyclic voltammograms and the thickness of lithium chloride film as a function of scan rate.

rates, the film thickness in $LiAlCl_4$-SO_2Cl_2-SO_2 solutions was found to be slightly higher than that obtained in $LiAlCl_4$-SO_2Cl_2 or $LiAlCl_4$-SO_2Cl_2-Cl_2 solutions.

Electrochemical oxidation of sulfuryl chloride.— Cyclic voltammograms (voltammogram B, Fig. 1) for the oxidation of $LiAlCl_4$-SO_2Cl_2 solutions at glassy carbon electrodes were similar to those obtained in $LiAlCl_4$-$SOCl_2$ solutions (9, 13). Thus, analogous to $LiAlCl_4$-$SOCl_2$ solutions, anodic peak V at ~ 4.6V and the sharp increase in anodic current at ~ 4.75V in these voltammograms (Fig. 1) may be regarded as due to the oxidation of $AlCl_4^-$ ions and SO_2Cl_2, respectively

$$AlCl_4^- \rightarrow AlCl_3 + \tfrac{1}{2} Cl_2 + e \qquad [6]$$

$$SO_2Cl_2 + AlCl_4^- \rightarrow SO_2Cl^+AlCl_4^- + \tfrac{1}{2} Cl_2 + e \qquad [7]$$

Thus, if the potential of the glassy carbon electrode is held at ~ 5V for few minutes before scanning it in the cathodic direction, the formation of chlorine at more positive potentials (Eq. [6] and [7]) causes an increase in peak height for the chlorine reduction peak (peak I) in the cyclic voltammograms. At the same time, aluminum chloride formed in Eq. [6] partially dissolves the lithium chloride film on the electrode surface and causes an overall increase in combined peak heights for peaks I and II.

Manuscript submitted Oct. 15, 1979; revised manuscript received Feb. 14, 1980. This was Paper 31 presented at the Los Angeles, California, Meeting of the Society, Oct. 14-19, 1979.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1981 JOURNAL. All discussions for the June 1981 Discussion Section should be submitted by Feb. 1, 1981.

Publication costs of this article were assisted by the U.S. Army Electronics Technology and Devices Laboratory (ERADCOM).

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